Note on Polymer-Mixed Solvent System
II. Application of the Previous Treatment

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Introduction

In order to investigate the state of the polymer molecules in the solvent, it is necessary to draw one's conclusion by summarizing the information obtained from various methods of physico-chemical measurements, i. e., viscosity, osmotic pressure, light scattering, swelling and others. This paper deals with discussions of the interaction exhibited by several polymer-mixed solvents systems from the results of these measurements. Employing the partial molal free energy expression obtained in Article I, the phenomenon that the first portions of the addition of non-solvent improve the solvent ability of the medium in some cases and the abnormality which arises in the cases in which one or both of the mixed solvents are an associated liquid, will be interpreted.

Relationship between Intrinsic Viscosity and Thermodynamic Quantity μ

We are going to focus our attention on one polymer molecule and consider the equilibrium between an effective volume pervaded by a polymer chain and its environments. As is seen in our treatment applied to the explanation of the Schulz's osmotic pressure equation,⁽¹⁾ the activity a_s of the solvent in the region occupied by a polymer molecule is given by

$$\ln a_s = \bar{F}_{1s}/RT = \ln(1-v_{2s}) + v_{2s} + \mu' v^2_{2s} + A v_{2s}{}^{1/3} - B v_{2s}, \qquad (1)$$

where $\Delta\bar{F}_{1s}$ is the partial molal free energy of solvent and v_{2s} the volume fraction of polymer, subscript s showing the spherical region in which a polymer molecule is distributed. A and B are constants somewhat dependent on molecular weight, solvent type, etc., and μ' is an interaction parameter, a little different from true thermodynamic quantity μ as was discussed⁽¹⁾ in our previous paper.

An analogous procedure can be applied to the polymer 3-mixed solvents 1 and 2 system, so long as the single liquid approximation may be permissible. Thus,

$$\ln a_s = \Delta\bar{F}_{0s}/RT = \ln(1-v_{3s}) + v_{3s} + \mu' v^2_{3s} + A v_{3s}{}^{1/3} - B v_{3s}, \qquad (1')$$

where μ' is supposed to be a little larger than $\mu_s + \mu_{30}$ used in Article 1 as mentioned above. $(\mu' = \mu_s' + \mu_{30})$. The above procedure is entirely equivalent to that of the swelling equilibrium. All the terms in the right-hand side of Eq. (1′) except $A v_{3s}{}^{1/3}$ are assumed to correspond to the dilution of a polymer molecule with the solvent. Thus, these must be replaced by the partial molal free energy expression derived in Article 1, although some modifications are still required due to the above restriction for the number of configurations. The relationship between intrinsic viscosity and thermodynamic quantity μ can, however, be derived as a rough approximation from Eq. (1′). If the single liquid approximation may be allowed, we may write for the condition of the equilibrium between the above two regions at infinite dilution.

$$\ln a_s = \Delta\bar{F}_{30}/RT = \ln(1-v_{3s}) + (1-B)v_{3s} + (\mu_s' + \mu_{30})v^2_{2s} + A v_{3s}{}^{1/3} = 0. \qquad (2)$$

Thus we can obtain the relation between v_{3s} and $\mu_s' + \mu_{30}$. The volume fraction v_{3s} in the spherical region is related to intrinsic viscosity $[\mu]$ as follows, including φ function representing the effective permeation of the flowing solvent through the domain of polymer chain in the Debye and Buche's treatment,⁽²⁾

$$[\mu] = [(\mu_r - 1)/c]_{c\to 0} = 0.0025\,\varphi/v_{3s}\rho, \qquad (3)$$

where c is the concentration in g. per litre and ρ the density of the polymer.

The above treatment is entirely equivalent to that of Flory who discussed the configurations of a polymer molecule in a binary polymer-solvent system.⁽³⁾ Although the true thermodynamic equilibrium between the above two regions is discussed for the single liquid approximation here, it is easily seen that the result obtained is reduced to the Flory's when his expression α, the factor by which linear dimension of the distribution of segments becomes larger than that of random flight configurations owing to long range interference is employed. However, further discussion concerning the problems of selective adsorption, volume effect of solvent, etc. may become possible when the free energy expressions in Article 1 are used. Comparison of this treatment with some viscosity data will be presented elsewhere in more detail.

Now the relation Eq. (2) is expressed as follows;

$$F(v_{3s}) = -(\mu'_s + \mu_{30})v^2_{3s}, \qquad (4)$$

where

$$\mu_{30} = (V_0/RT)[-\theta/(1+\theta)^2 \times A_{12} + 1/(1+\theta) \times A_{13} + \theta(1+\theta) \times A_{23}]. \qquad (5)$$

(The notation of these equations is similar to what was employed in Article 1.)

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(1) T. Kawai, This Bulletin, **24**, 69 (1951).

(2) P. Debye and A. M. Buche, *J. Chem. Phys.*, **16**, 573 (1948).

(3) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

Differentiating Eq. (4) with respect to θ, if $F(v_{3s})$ and μ'_s can be assumed to be independent of θ(4);

$$d\{F(v_{3s})/v^2_{3s}\}/dv_{3s}\times dv_{3s}/d\theta=d\mu_{30}/d\theta. \qquad (6)$$

This result shows that the maximum in intrinsic viscosity and the minimum in thermodynamic quantity μ appear in the ratio θ_c of volume fraction of liquid 2 to that of liquid 1, at which the following condition is satisfied,

$$d\mu_{30}/d\theta=-(1-\theta_c)/(1+\theta_c)\times\mu_{12}+\mu_{23}-\mu_{13}=0, \qquad (7)$$

where $\mu_{12}=(V_0/RT)A_{12}$, $\mu_{13}=(V_0/RT)A_{13}$, $\mu_{23}=(V_0/RT)A_{23}$.

Here we assume liquid 1 is solvent ($\mu_{13}<1/2$), and liquid 2 non-solvent ($\mu_{23}>1/2$). Then, the sulution of this equation (7) can afford physical meaning only when $(\mu_{23}-\mu_{13})/\mu_{12}<1$. Namely, when $(\mu_{23}-\mu_{13})/\mu_{12}>1$, the solvent ability of the medium decreases uniformly with increasing θ ($d\mu_{30}/d\theta>0$). When $(\mu_{23}-\mu_{13})/\mu_{12}<1$, the solvent ability of the medium is improved until θ_c, at which Eq. (7) is satisfied, and since then it decreases as θ increases. For the same value of μ_{12}, the larger the $(\mu_{23}-\mu_{13})$ values, the smaller the θ_c. In other words, when liquid 1 has a stronger solvent power and liquid 2 has a stronger precipitating power, the solvent power of the mixture shows a maximum value at smaller content of non-solvent and vice versa. It must be noted, however, that the contribution of μ_{12} to the values of μ_{30} should be considered also. For the same values of $(\mu_{23}-\mu_{13})$, the larger the value of μ_{12}, the larger the θ_c. Besides, as is seen from Eq. (5), the solvent ability of the mixture is improved more effectively by larger values of μ_{12}. Various methods of estimation of the interaction parameters, μ_{12}, μ_{13}, and μ_{23} for a few systems are presented in the next section.

Discussion for Several Actual Systems

The parameter μ_{30}, a measure of the energetical interaction in these ternary systems, consists of three parts as seen in Eq. (5). In this connection, these three parameters μ_{12}, μ_{13}, and μ_{23} must be estimated. When polymer 3 is soluble in liquids 1 and 2 ($\mu_s+\mu_{13}<1/2$, $\mu_s+\mu_{23}<1/2$), the quantities μ_{13} and μ_{23} can be evaluated from osmotic pressure measurements. And when one of the two liquids is non-solvent ($\mu_s+\mu_{13}>1/2$, or $\mu_s+\mu_{23}>1/2$), we must calculate the values of μ_{13} or μ_{23} from swelling measurements. The parameter μ_{12} can be evaluated from vapor pressure data for the binary system liquid 1-liquid 2 as follows: When the entropy of mixing in this system may be assumed to be ideal,(5) we may write

$$\ln\gamma_1=\ln a_1-\ln x_1=\Delta\bar{H}_1/RT=(V_1/RT)A_{12}v_2^2 \qquad (8)$$

$$\ln\gamma_2=\ln a_2-\ln x_2=\Delta\bar{H}_2/RT=(V_2/RT)A_{12}v_1^2, \qquad (8')$$

where the a's are the activity, the γ's the activity coefficient, and the x's the molar fraction of each component. Therefore, if $\ln\gamma_1$, which can be usually obtained from vapor pressure data, is plotted against v_2^2, and similarly $\ln\gamma_2$ against v_1^2, each set of points will generally fall on a straight line. The slope of the line gives the values of $(V_1/RT)A_{12}$ and $(V_2/RT)A_{12}$ respectively. Considering the approximation used in deriving Eq. (7), we may adopt the mean value of them as $(V_0/RT)A_{12}$. Thus, we can estimate μ_{13}, μ_{23} and μ_{12} separately.

In this connection the systematic experiments involving osmotic pressure, viscosity, swelling and the other measurements should be required to investigate the interaction of polymer and mixed solvents. Since such series of systematic experimental results have not been presented for any of the polymer-mixed solvents systems, it is necessary to estimate the μ's from the experimental data involving only one or two of the above various measurements.

Now, in spite of the weakness that we can not determine uniquely the effect of the solvents in such a three-components system, the dilution ratio, which is determined by the addition of a non-solvent to a polymer solution of a standard concentration until phase separation begins, may also be useful to estimate roughly the μ's employing condition as follows;

$$\mu_s+\mu_{30}=\mu_s+[-\theta/(1+\theta)^2\times\mu_{12}+1/(1+\theta)\times\mu_{13}+\theta/(1+\theta)\times\mu_{23}]\fallingdotseq 1/2. \qquad (9)$$

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(4) The constant A in Eq. (2) is not always independent of θ as was seen from its expression. This assumption, however, may be permissible since its dependency on θ does not have any notable effect on our result.

(5) This is true for two non-polar liquids systems, so long as molal volumes of the two liquids do not differ very largely from each other. (see Hildebrand; "Solubility of Non-electrolytes", 3rd Ed. Reinfold Publishing Corp., New York, 1950)

This relationship (9) and Eq. (7) in the preceding section can be used in estimating the μ's respectively.

Employing the methods mentioned above, we are going to discuss the interaction of polymer and two liquids for several actual cases. Yoshioka measured viscosity of polyvinyl acetate in various mixed solvents.(6) Considering the abnormality in the systems involving some associated liquids as components, these systems are to be divided into three; namely, polymer 3-associated liquid 1-non-associated liquid 2, polymer 3-associated liquids 1 and 2, and polymer 3-non-associated liquids 1 and 2.

1. Polymer 3-Associated Liquids 1 and 2

(a) Polyvinyl Acetate-Acetone-Water System.—From the osmotic data(7)(8) for polyvinyl acetate-pure acetone system at different temperatures, there is obtained for the interaction parameters $\mu_s=0.47$, $\mu_{13}=-0.04$. According to Eq.(27) in Article 1, $\mu_s=1/2-1/2y$, and thus, the abnormally large value of μ_s was acceptable, although quantitative discussion is impossible owing to the rough approximate treatment in Article 1. Actually, this value of μ_s is extraordinarily larger than that estimated theoretically for a fairly flexible chain(9) and expected also from many experimental facts. Employing the Yoshioka's data, we obtain

from Eq. (7) $0.9\,\mu_{12}-0.04-\mu_{23}=0$

(the condition for $[\eta]_{\max.}$, $\theta/(1+\theta)=0.05$(10)), (10)

and

from Eq. (9) $-0.197\,\mu_{12}-0.029+0.27\,\mu_{23}=0.03$

(the condition for the precipitating point, $\theta/(1+\theta)=0.27$(6) $\mu_s=0.47$(11)) (11)

From Eqs. (10) and (11), $\mu_{12}=1.53$, $\mu_{23}=1.33$. Adopting these values for μ_{12}, μ_{13} and μ_{23}, the $\mu_s+\mu_{30}$ values are calculated against $\theta/(1+\theta)$ in Fig. 1, compared with those obtained from the Endo's osmotic data,(8) and with intrinsic viscosity(6) for various contents of water. On the other hand, the μ_{12} value calculated from the vapor pressure data in the International Critical Table gives extremely large value ($\mu_{12}=7.38$) when Eq. (8) and (8′) are used, but our treatment for two associated liquids system bring out an appropriate value for μ_{12}. From Eq. (26) in Article 1,

$$\ln a_1=\ln v_1+(1-y/x)v_2+\mu_{12}v_2^2 \qquad (12)$$

If we plot $(\ln a_1-\ln v_1)/v_2$ against v_2, the points fall on a line as given in Fig. 2. The slope of the line gives $\mu_{12}=1.45$. The estimation of y/x by exteraporation to $v_3=0$ affords a reasonable value ($y/x=1.5$(12)).

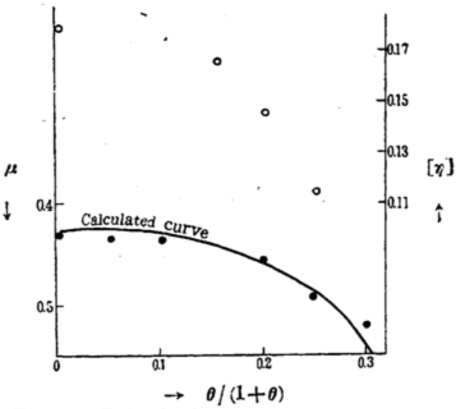

Fig. 1.—Polyvinyl acetate-acetone-water system.

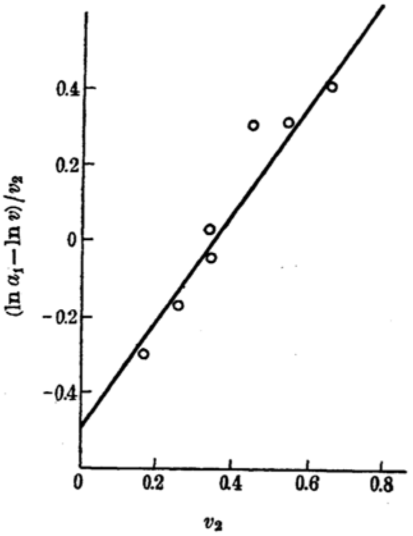

Fig. 2.—An example of calculation of μ_{12} (acetone-water system $\mu_{12}=1.447$).

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(6) Yoshioka, *J. Chem. Soc. Japan*, **72**, 8 (1951).

(7) G. Browning, J. D. Ferry, *J. Chem. Phys.*, **17**, 1107 (1949).

(8) K. Endo, *J. Chem. Soc. Japan*, **71**, 232 (1950).

(9) B. H. Zimm, A. C. S. Meeting, Sept. (1947) (P. Doty, M. Brownstein and W. Schlener, *J. Phys. Coll.* Chem., **53**, 243 (1949).)

(10) K. Yoshioka, This Bulletin, **23**, 60 (1950).

(11) Comparing Eq. (36) with Eq. (27) in Article I, it is seen that the adoption of this value for μ_s is not unfounded.

(12) Although both x and y may be considerably large, the values of y/x are anticipated in the range from 0.1 to 1.0.

(b) Polyvinyl Acetate-Methanol-Water System.—Endo measured osmotic pressure of polyvinyl acetate in methanol-water mixture of several compositions.(13) The $\mu_s+\mu_{30}$ values for various contents of water are calculated from his data as is shown in Fig. 3. Since the results of the measurements at different temperatures are not yet published, μ_s and μ_{30} cannot be evaluated separately. It may be said, however, from the information of temperature dependence of intrinsic viscosity(13) that μ_{30} is positive even at θ_c for $[\eta]_{\max.}$ in this system. Moreover, the μ_s value is supposed to be not far from $0.45\sim0.47$ and this is acceptable from our procedure as in the case (a). Substituting these values of $\mu_s+\mu_{30}$ for θ in Eq. (9), we can obtain five equations, from which the most appropriate values for the μ's are determined as follows, $\mu_s+\mu_{13}=0.486$, $\mu_s+\mu_{23}=0.714$, $\mu_{12}=0.30$. Then, the composition at which intrinsic viscosity shows a maximum is calculated from Eq. (7) as $\theta=13.6$, $\theta/(1+\theta)=0.12$, showing a satisfactory agreement with experimental results ($\theta/(1+\theta)=0.15$ by Matsumoto,(14) $\theta/(1+\theta)=0.20$ by Endo(13)). Although the change of $\mu_s+\mu_{30}$ with $\theta/(1+\theta)$ is comparatively small in this case, the Endo's measurements(13) show that intrinsic viscosity changes with $\theta/(1+\theta)$ considerably as is shown in Fig. 3. Furthermore, Endo pointed out that in this system the second virial coefficient A_2 in the osmotic pressure equation depends on molecular weight of the polymer to a remarkable degree. These abnormalities cannot yet be explained, but some suggestions may be given for the solution of these problems by our procedure for polymer-two associated liquids system in Article 1.

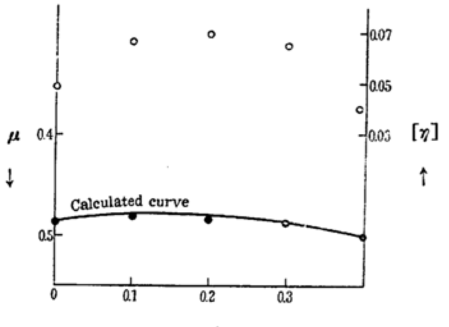

Fig. 3.—Polyvinyl acetate-methanol-water system.

(2) Polymer 3-Associated liquid 1-Non-associated Liquid 2 System

The above calculation involves implicitly an assumption that the μ_s value in polymer-mixed solvents system equals that of the polymer-one of the mixed solvents system. As can be understood from Eqs. (27) and (36) in Article 1, this assumption may be acceptable for polymer-two associated liquids system, but Eq. (32) in Article 1 shows that it may not be applicable to the present system. It may be said, however, that this assumption may not cause a remarkable error when the associated liquid is solvent (not non-solvent) as easily seen from Eqs. (31) and (27) in Article 1. Actually, the following treatment considering the heat term only can be an explanation of the polymer-mixed solvents interaction in this system, showing a good agreement with experimental data.

(a) Polyvinyl Acetate-Acetone-Ether System.—The binary system of acetone-ether does not show such specific interaction as acetone-water and methanol-water systems and Eq. (8) or (8′) holds its validity. Thus, the μ_{12} value may be calculated from vapor pressure data in International Critical Table ($\mu_{12}=0.54$). Employing this value for μ_{12} and -0.04 for μ_{13}, we can obtain $\mu_{23}=0.34$ from Eq. (7) for the condition of $[\mu]_{\max.}$ $(\theta_c/(1+\theta_c)=0.15.)$(6) The $\mu_s+\mu_{30}$ values calculated from these values μ_{12}, μ_{13} and μ_{23} show a good correspondence to intrinsic viscosity for varying compositions of the mixed solvents as is shown in Fig. 4, i. e., the solvent ability of the medium decreases slowly as the content of ether increases without a conspicuous maximum. Obviously, this is due to the small value of μ_{23}. It is not appropriate to say that ether is non-solvent for polyvinyl acetate.

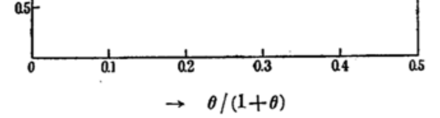

Fig. 4.—Polyvinyl acetate-acetone-ether system.

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(13) K. Endo, *J. Chem. Soc. Japan*, **72**, 883 (1951).

(14) S. Matsumoto, *Chem. of High Polymer, Japan*, **6**, 179 (1949).

(b) Polyvinyl Chloride-Acetone-Carbon Disulfide System.—As a special case where polymer is soluble only in a certain range of composition of liquids 1 and 2, osmotic pressure, viscosity and swelling are measured in this system by Ishikawa and Kawai.(15) In Fig. 5 the values of μ and $[\mu]$ obtained from the above three measurements are compared with $\mu_s+\mu_{30}$ calculated from our procedure by adopting $\mu_{12}=0.8$, $\mu_s+\mu_{13}=0.534$, $\mu_s+\mu_{23}=0.650$. The values of $\mu_s+\mu_{13}$ and $\mu_s+\mu_{23}$ are evaluated from the swelling measurement. Although the μ_{12} value calculated from vapor pressure data(16) is 1.04, we adopt $\mu_{12}=0.8$, because this value shows rather better agreement with the experimental facts. Namely, employing this value, there is obtained $\theta/(1+\theta)=0.05$ or 0.78 for the precipitating point and $\theta/(1+\theta)=0.52$ for $[\mu]_{\max}$.

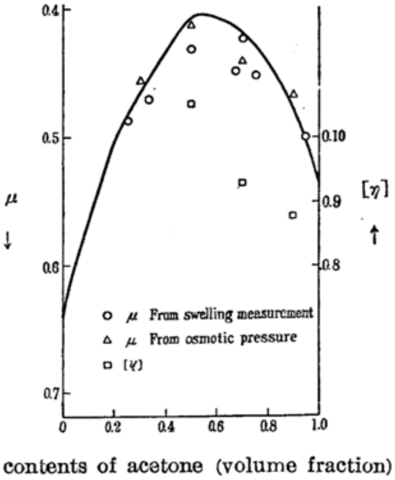

Fig. 5.—Polyvinyl chloride-acetone-carbon disulfide system.

Finally, this system is not a special one but is assumed to be one of the systems in which the solvent power of the medium is improved by the addition of diluent until a certain composition is reached, whereas in this case, the polymer is not soluble in the individual constituents of this mixture.(17)

(c) Polyvinyl Acetate-Acetone-Petroleum Benzin System.—Combining Eq. (7) for the condition of $[\mu]_{\max}$. ($\theta/(1+\theta)=0.13^{(6)}$) and Eq. (9) for that of the precipitating point ($\theta/(1+\theta)=0.45^{(6)}$), there is obtained $\mu_{12}=0.819$, $\mu_{23}=0.566$, ($\mu_{13}=-0.04$). Considering the approximate treatment used here, it may be questionable to determine the μ's from these two conditions only. Further discussion may, however, be impossible also from the fact that petroleum benzin is a mixture of heptane, hexane and others. In practice, a fairly good correspondence is obtained between thus calculated $\mu_s+\mu_{30}$ and intrinsic viscosity for varying contents of petroleum benzin, as is shown in Fig. 6.

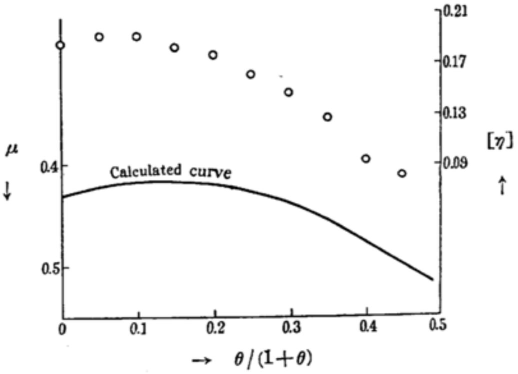

Fig. 6.—Polyvinyl acetate-acetone-petroleum benzin system.

(3) Polymer-3-Non-Associated Liquids 1 and 2

(a) Polyvinyl Acetate-Benzene-Petroleum Benzin System.—From the Nakajima's osmotic data,(18) $\mu_s+\mu_{31}=0.319$ and $\mu_s+\mu_{30}=0.432$ at $\theta/(1+\theta)=0.30$. From these data, calculation follows that $\mu_{12}=0.438$, $\mu_{13}=-0.151$, $\mu_{23}=0.566$, where μ_{23} is that obtained in the case 2(c). Substitution of these values

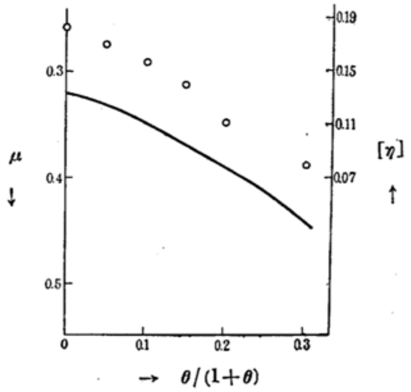

Fig. 7.—Polyvinyl acetone-benzene-petroleum benzin system.

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(15) K. Ishikawa and T. Kawai, *J. Chem. Soc. Japan Ind. Chem. Section*, **55**, 173 (1952).

(16) J. V. Zawidzki, *Z. physik. Chem.*, **35**, 129 (1900).

(17) This phenomenon, known as "cosolvency", is seen also in a few other systems, for instance, polystylene-acetone-methylcyclohexane system. (S. P. G. Colombo and H. Mark, *J. Polymer Sci.*, **6**, 295 (1951).)

(18) A. Nakajima, *Chem. of high Polymer, Japan*, **6**, 451 (1949).

for μ_{12}, μ_{13}, and μ_{23} in Eq. (7) gives a negative value for θ_c, which is meaningless in a physical sense. This agrees with the experimental fact that $[\mu]$ decreases uniformly with addition of non-solvent in this system. In Fig. 7, the calculated $\mu_x+\mu_{30}$ values are plotted against $\theta/(1+\theta)$, being compared with the intrinsic viscosity data.(6) Furthermore, the Vold's data(19) of vapor pressure in benzene-heptane system give $\delta_1-\delta_2=2.493$, where δ_1 and δ_2 are the Hildebrand's solubility parameter(20) of the individual liquids. Assuming $V_0=100$, μ_{12} can be estimated as 0.428 from this value of $(\delta_1-\delta_2)$, affording a good coincidence with the above estimation.

Conclusion

Considering the two assumptions which were introduced by Scott in his treatment of phase equilibrium in a ternary system of polymer and two liquids, more general free energy expression to correlate much of the experimental data has been derived in Article 1. When some of the three components are polar, it may be anticipated that the deviation from the Scott's treatment due to invalidity of the assumption (a) is especially important. Thus, our modification of his treatment was checked here with some experimental results principally with regard to the assumption (a). Furthermore, the assumption (b) is far from true especially when one or both of the mixed solvents are associated liquid, but even in such cases, all complicated factors are covered by an approximate method in the present treatment, although this approximate treatment must be discussed in more detail. Actually, the present treatment is applicable to many ternary systems with a fair degree of accuracy. The characteristics of each system are well expressed by the interaction parameters μ_{12}, μ_{13}, and μ_{23}. Thus, the phenomenon that the medium involving non-solvent to some extent behaves as a better solvent than the pure solvent and the abnormal behavior in the systems containing associated liquids as one or two components can be understood from our procedure in Article 1.

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(19) R. D. Vold, *J. Am. Chem. Soc.* **59**, 1515 (1937).

(20) The Hildebrand's parameter δ_i represents the square root of internal pressure (or "cohesive energy density") $(\Delta E^v{}_i/V_i)^{1/2}$, where $\Delta E^v{}_i$ is the energy of vaporization and V_i the molal volume of liquid i. When the assumption of the "geometric mean' is permissible as in this system where the both two liquids are non-polar, $\Delta H^M_{12}=V_0(\delta_1-\delta_2)^2v_1v_2$, *i. e.*, $\mu_{12}=V_0(\delta_1-\delta_2)^2$.